



The role of biochar porosity and surface functionality in augmenting hydrologic properties of a sandy soil

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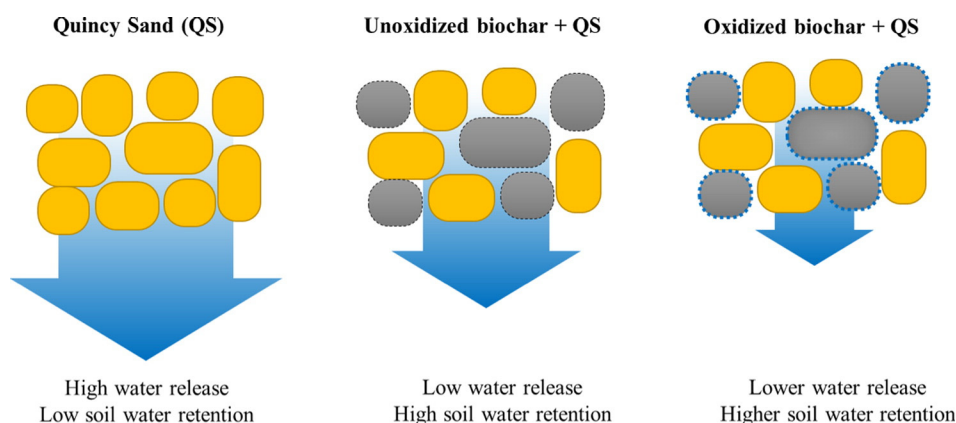
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HIGHLIGHTS

- Oxidized biochars retain more water than unoxidized ones.
- Air oxidation of biochar is a suitable way to enhance water holding capacity of biochar and its blends with soils.
- There is a positive correlation between total acidic functional groups on the surface of biochar and soil water retention.
- The capability of biochar to retain soil water is a function of the combination of its porosity and surface functionality.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports studies to elucidate the potential relationships between porosity and surface functionality of biochar and soil water retention characteristics. The biochars studied were produced from pine wood (PW), hybrid poplar wood (HP), and pine bark (PB) at temperatures of 350 °C and 600 °C. The resulting materials were then oxidized under air at 250 °C to generate oxygenated functional groups on the surface. All biochar were thoroughly characterized (surface and bulk properties) and their hydrological properties measured in blends with Quincy sand. We prepared 39 microcosms for this study to examine the effect of biochar functionalities and porosity on the hydro-physical properties of Quincy sand. Each biochar was thoroughly mixed with the soil at 20 g kg⁻¹. The field capacity, wilting point, and total available soil moisture of the bio-char/Quincy sand mixtures were measured for both dry and wet ranges. The soil water potentials and soil water contents were fitted using the model of van Genuchten. Our results indicated that the amount of oxygenated functional groups on the surface of biochars clearly differentiated the biochars in terms of hydrophilicity, with the oxidized biochars being superior, followed by the low-temperature biochars, while the high temperature biochars possessed lowest hydrophilicity. As a result, oxidized biochars exhibited better wettability compared to unoxidized biochars,

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regardless their feedstock source. Significant correlation occurred between the total acidic functional groups on biochar surface and water contents at different matric potentials. Over a wide range of soil water potentials, oxidized biochar-soil mixtures held more water than the unoxidized biochar-soil mixtures except in the region between -0.1 and -5 kPa of ψ , which is near saturation. Soil water contents at different matric potentials were significantly inter-correlated ($P < 0.01$) and correlated with bulk densities of biochar-amended soil samples.

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1. Introduction

Biochar application to soils is not a new concept; it was used successfully by generations of indigenous farmers in the Amazon basin (Maia et al., 2011). Accumulation of bulky quantities of biochar increased soil agronomic quality and formed what is known as Amazonian Dark Earths (or *Terra Preta*) which are still highly valued soils for agricultural and horticultural use (Verheijen et al., 2010). Biochar, as a term, is reserved for any carbon-enriched porous material that has been chemically and structurally altered through thermo-decomposition via anaerobic pyrolysis and that is used specifically as a soil amendment (Forbes et al., 2006; Lehmann et al., 2006). Properties of biochar depend on the original biomass (chemical composition, ash content, particle size), the production conditions (temperature, residence time, oxidative conditions), the pre-treatment procedures (drying, crushing), and the post-treatment processes (i.e. activation method) (Copeland et al., 2008; Lehmann and Joseph, 2009).

Use of biochar is a sustainable option to provide long-lasting improvements in soil fertility (Lehmann et al., 2003; J.M. Novak et al., 2009a), especially in sandy soils where sustainable agriculture faces large constraints due to low water holding capacity, and high leaching of soil nutrients (Uzoma et al., 2011). Because of its ability to retain nutrients and to improve soil water holding capacity, biochar soil application can be used to overcome some of the limitations faced when land farming sandy soils (i.e. additional requirements for artificial fertilizers and intensive irrigation) providing a promising soil management option for these conditions. Positive effects of biochar on soil properties and plant growth in sandy soil are well documented (Basso et al., 2013; Uzoma et al., 2011). Recent studies have shown that biochar soil additions increase pH of acidic, enhance cation exchange capacity (CEC), increase soil water-holding capacity, modify soil bulk density, and increase exchangeable basic cations soils (Basso et al., 2013; J. Novak et al., 2009b; Liang et al., 2006; Sika, 2012).

While greater scientific attention has resulted in an increasing number of biochar publications, there is still a need for further research with respect to how the biochar affects some of the limiting factors of agricultural production in sandy soils. Little work has been done to address the use of biochar application to enhance the hydrological properties of these soils. In addition, there is a need for research that investigates the relationship between the surface chemistry of biochar and water hydrological characteristics of biochar amended soils. In particular, the effects of biochar porosity and surface functionalities' effects on the hydro-physical properties of a sandy soil are relatively unknown compared to other common parameters (e.g. application rate, pyrolysis temperature, feedstock source). Hence, the goal of this study is to evaluate the effect of biochar bulk and surface properties on hydro-physical properties of Quincy sand-biochar blends, as well as to explore the potential of oxidized biochar to retain water in the Quincy sand.

2. Material and methods

2.1. Biochar preparation

Biochars were produced at the biomass thermochemical conversion laboratory at Washington State University from Pine Wood, Pine Bark and Poplar Wood. The Lab scale spoon reactor, Fig. 1, was operated at two pyrolysis temperatures: 350 °C and 600 °C representative of the

lower and upper pyrolysis thresholds for biochar formation. More details on the production methods are shown in Section 1 of the supplementary material. Here, biochars are denoted as PW for the pine wood feedstock and PW-350, and PW-600 for the resulting unoxidized biochars created at 350 and 600 °C, respectively. The oxidized samples are abbreviated as AO referring to air oxidation. Similar abbreviation procedure was applied for the pine bark (PB) and hybrid poplar wood (HP) batches.

2.2. Biochar characterization

The bulk and surface characterization of the biochars studied in this paper were reported elsewhere (Suliman et al., 2016a,b). A brief description is shown in the supplementary material (Section 2). Some of the most important properties of the 'biochar' tested that are relevant for this study are summarized in Table 1.

2.3. Soil

The Quincy sand (QS) was used in this study because it is present on nearly 285,000 ha in Washington, Oregon, and Idaho, and is an agriculturally important soil in the Pacific Northwest region of the US (<http://www.nrcs.usda.gov/wps/portal/nrcs/soilsurvey/soils/survey/state/>). The sand was collected, air-dried, and sieved through a 2 mm mesh. Some selected physical and chemical characteristics are shown in Table 2. To measure the soil zeta potential, 5 g of the soil was added to 100 ml of deionized water and agitated on an orbital shaker for 6 h at 25 °C. The aliquot of the supernatant was then collected (decanted from the container) and analyzed by Nano-Zetasizer 3000 (Malvern Instruments Ltd., Malvern, UK).

2.4. Experimental design

Thirty nine microcosms were prepared for this study to examine the effect of biochar on hydro-physical properties of Quincy sand. Each biochar was thoroughly mixed with the soil at a rate of 20 g biochar kg⁻¹ soil. The mixing rate was calculated by assuming 15 cm and 1.5 g cm⁻³ for soil depth and bulk density, respectively. Three replicates of 30 g of each mixture were then packed into plastic containers. Bulk density, porosity, organic matter, pH, and EC were determined for biochar-soil mixtures using the methods described previously in Section 2.2 for the biochar. These mixtures were abbreviated as QS, QS-HP350-UO, QS-HP600-UO representing the soil control (Quincy sand alone), soil with unoxidized HP biochar produced at 350 °C (HP350), soil with unoxidized HP biochar produced at 600 °C, respectively. The same abbreviation were utilized for soil with unoxidized PW and PB biochars, and for oxidized samples but with adding AO.

2.5. Soil hydraulic measurements

To evaluate the influence of biochar on the water relations of sandy soil, consideration must be given to the effect on field capacity, wilting point and total available soil moisture. In the present study, soil water retention was measured on intact soil microcosms for both dry and wet ranges. A T5 Tensiometer (UMS GmbH, Munich, Germany) was used to measure metric potential above -100 kPa, whereas a WP4C

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